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Causes of Polyester Resin - Filler Surfacing Systems Failures

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Synopsis: For surfacings the unsaturated polyester - filler systems are used in a considerable extent. In some cases failures occur even after a considerable period (blisters, cracks, etc.). These failures are due to physical, chemical and microbiological effects, a detailed analysis of various causes of these failures being given. Physical failures are due to the shrinkage of the binder, thermal effects, composite behavior of the surfacing, exceeding of mechanical properties, unsuitable structural composition, effects of unsuitable base, environment and raw materials, aging of binder and inadequate treatment of the base. Chemical failures are due primarily to the moisture content of the base or of raw materials which inhibits polymerization and enhances oxidation and hydrolysis of the resin; polymerization is influenced heavily also by various shortcomings of raw materials and technology.

Thorough knowledge of all circumstances influencing the properties of UP systems is the necessary prerequisite of a successful application of surfacings (in the form of cast systems, screeds, glass reinforced plastics, polymer concretes). Analysis of the causes of various failures of polyester systems which have occurred in construction practice is a valuable source of information in this respect.

Key Words: Composite materials, resin concretes (screeds, cast surfacings), surfacings, floorings, polyester resins, failures.

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INTRODUCTION

Apart from a number of successfully applied floorings and surfacings based on unsaturated polyester (UP) resins,[1] whose performance has been faultless for a number of years, there are some defects of these systems which repeatedly occur. These defects manifest themselves after the elapse of periods from the execution of the surfacing which vary from several days to several years. There appear dense micro- or macro-cracks on the surface (crackling), furrowing of the surface (Fig. 1), rare but wide cracks passing through the whole surfacing, accompanied with a bowl-like rising of edges (Fig. 2), and rising of edges along expansion joints and all ends in general (Fig. 3). In some cases blisters appear of various diameters, ranging from millimeters to dozens of centimeters (Fig. 4). Sometimes a layer does not harden properly or softens subsequently, thus facilitating the perforation of the surfacing. In yet other cases, the surfacing separates from the base or the individual layers separate from one another. Some defects are due to the structural system used and are often independent of the type of binding agent; others depend on the properties of the polyester resin used and are due to an unsuitable design or technological defects.

It is desirable, therefore, to sum up our knowledge of polyester systems and analyze the reasons and causes of the defects to prevent their repetition.

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[1] UP resins are used either as fundamental components of the material, when they form the flooring system either alone or lightly filled with fibrous or fine-particle granular filler, or as a binder (matrix) of granular or fibrillate mixes (fillers) to form surfacings of a considerable load bearing capacity. In the former case we speak about laminated surfacings (laminated screeds) if a fibrillate filler is used, about flooring screeds if a granular filler is used, or about case (poured) surfacings if the quota of the filler is very low or equals zero (in general these cases involve filled binders). In the latter case we speak - in accordance with the layer thickness and, or consequently, the maximum particle size - about resin concretes or resin mortars (in general - bonded fillers). Both systems differ not only in composition and appearance but also by a considerably different mechanical, physical, and chemical behavior (2).

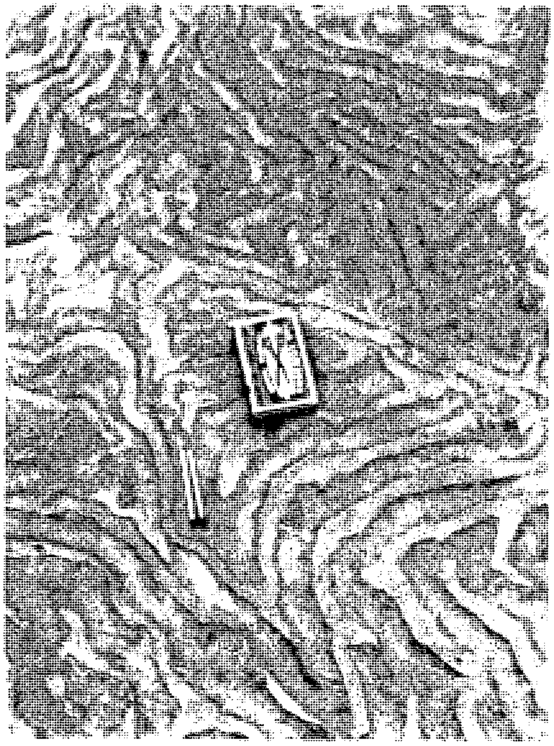

Fig. 1. Furrowing of the surface of excessively diluted UP surfacing.

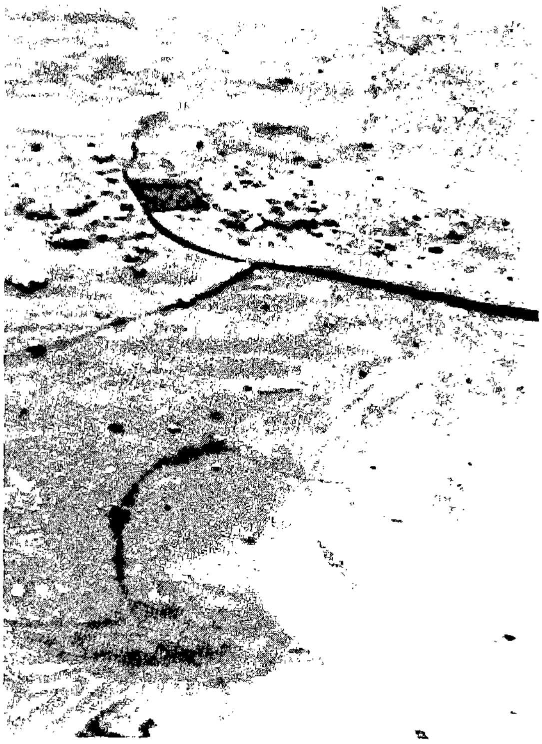

Fig. 2. Wide cracks with bowl-like rising of edges.

Fig. 3. Cracks and edge rising at the end of flooring.

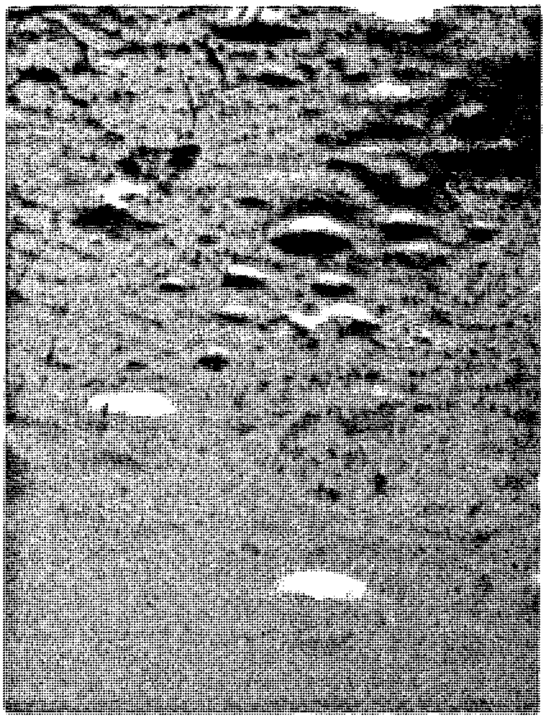

Fig. 4. Blisters due to enclosed moisture.

The factors causing defects, although they often act in unison, can be classified, with the usual risk of simplification, into the following groups:

(1) physical (mechanical and structural) factors,
(2) chemical factors,
(3) microbiological factors.

PHYSICAL FACTORS

The UP resin-based surfacings are structurally nonhomogeneous, porous systems influenced, as such, to a considerable extent by the properties of their components (filler, binder). Moreover, the surfacing itself is a composite system whose solid phases have markedly different properties. At the interfaces of the individual layers, which are of the most varied character and have considerably different physical properties, as well as structural composition, deformation compatibility is essential. In the structural assessment of the whole system, the influence of the type of resin used is obviously of minor importance, the majority of the following considerations being generally valid also for the systems of other resins.

Binder Shrinkage

The polymerization of UP resins is a heavily exothermic process (some 60 cal/g in 2 hours), which is accompanied with its shrinkage of 5 to 8 percent by volume. The segregated (dispersed) filler in the binding agent speedily reduces the shrinkage of the system until the state of aggregation of the filler is attained; afterwards, the shrinkage is only mildly reduced in accordance with the extent of compaction (Fig. 5).

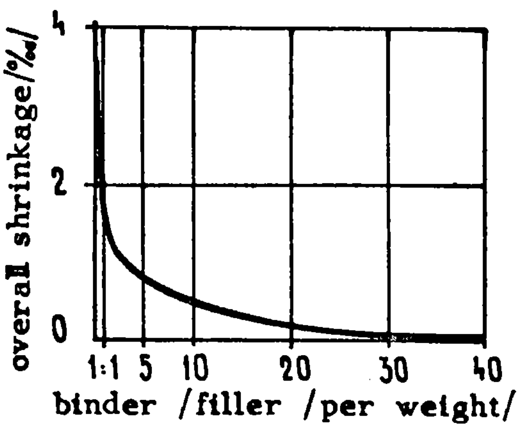

Fig. 5. Linear shrinkage of UP systems.

The shrinkage proceeds most quickly in the first phase, until gelation sets in, and lasts, slowly attenuating, for a long time (for weeks or months, in accordance with the type of resin). In the structure of the hardening layer, in the same way as in the composite system as a whole, stresses originate, viz., tensile stresses in the matrix (resin), compressive stresses in the filler, and shear stresses at their contact surfaces and at the contact surface of the adjoining layer (base). The stresses due to the shrinkage of the matrix attain, according to experimental tests (4,6), at least 2,5 - 3,0 MPa for the matrix of a tensile strength of over 30 MPa, and of an ultimate deformation of some 1 percent; they can attain, however, in accordance with the technology used, even the ultimate strength. The shear stresses attain, according to some investigations (5,7), 27-15 percent of normal tensile stresses for the usual ratio of the moduli of elasticity of the matrix and filler at 1:10.

In this respect, only such shrinkage of the matrix is permissible as enables, with the given technology, the relaxation of the stresses due to the creep of the individual phases or parts of the system. For this the following factors are decisive: the hardening speed (the slower the polymerization, the more favorable the state of stress of the system due to shrinkage), the choice of the binder components (it is preferable, if the growth of viscosity is slower than shrinkage, i.e., if long linear chains are formed before to the origin of cross links - Fig. 6) and the thickness of the layer of the binding agent (matrix) between the filler particles (the thinner, the better).

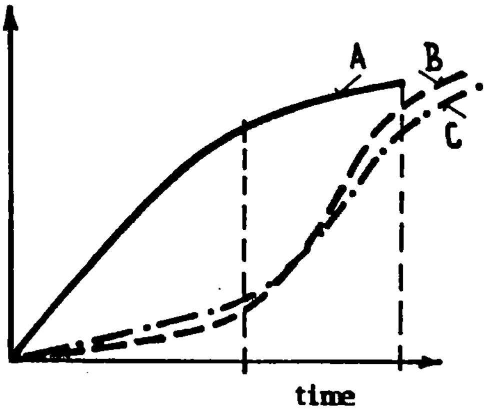

Fig. 6. Ideal course of properties during polymerization.
(A) shrinkage (polymerization);
(B) strength; (C) modulus of elasticity

Also a certain (closed) porosity of the system is favorable (1,2); it results, apart from the reduction of the amount of the matrix required, also, in a reduction of the thickness of its connecting links. Moreover, the inner voids enable considerable deformations of the connecting links without giving rise to major stresses: according to experimental investigations (6) the characteristic stresses in models with pores were 12 percent lower, the overall stress reduction amounting to more than 15 percent.

If the stresses within the system exceed any of the instantaneous magnitudes of its strengths (particularly if the polymerization proceeds at an excessive speed), microfailures of the structure can occur which, in a later phase and for other reasons, may give rise to an overall failure or reduction of the life of the system, not only due to the effect of aggressive environment or atmospheric factors, but also due to internal chemical processes which will be subsequently described further on. However, macrofailure, also, may occur (e.g., the separation of the individual layers of the system or the origin of large, widely opened cracks) even after several years, as a result of the exhaust of the strength of the material by the stresses due to shrinkage, often in combination with some other factors, e.g., effect of temperature.

The shear stresses due to the shrinkage in the contact joint are higher, the greater the relative thickness of the hardening layer is. Since the ultimate shear deformation of the adjoining layers is independent of the thickness of the hardening layer, the probability of the failure at the joint is directly proportionate to it. This is of importance particularly for the systems with no or little filler (with a great overall shrinkage).

According to the above analysis the prevention of the failure due to the shrinkage of UP systems requires that: (a) the layer of the matrix in the structure as well as in the whole surfacing be as thin as possible. (In the case of aggregated systems, e.g., PC, it means the use of dense composition aggregate, with the binder: filler ratio of 1 : 7 to 1 : 12 by weight, without the limitation of layer thickness; in the case of segregated systems, e.g., screeds and cast floors, it means the application of a minimum thickness layer since the thickness of over 2 mm already means a potential danger of the origin of failure), and (b) the shrinkage process be distributed over a period as long as possible (a minimum of 24 hours; excessive shortening is pronouncedly harmful to the quality and life expectancy of the flooring material).[2]

Thermal Effects (Expansion)

The coefficient of thermal elongation of neat UP resin, viz., 6 - 11 x $10^{-5}/^{o}C$, when compared with the coefficients of other materials with which the resin comes into contact in the systems under consideration, is many times higher, almost of a higher order. Any change of temperature from the "birth" temperature (i.e., the temperature at which the polymerization of the resin has taken place) gives rise to high inner stresses in the structure of the layer and in the whole flooring system. In case of sudden changes of temperature (shocks) these stresses can hardly be sustained without failure.

In a structure of resin concrete with quartzite filler particles a difference in linear deformation of filler and binder of 0,072 percent will occur with a temperature change of 10°C and a difference of volume deformation of 0.216 percent. In line with the experiments mentioned above, in "Binder Shrinkage", a change of temperature of 10° C will result in a stress of the order of 5 MPa of opposite signs in the filler and in the binder, and a shear stress in the contact joint of both components of some 0.7 - 1.3 MPa, the magnitude depending on the velocity of temperature change. The higher the thermal capacity of the surfacing the less it is vulnerable to temperature changes. With regard to the relatively high insulation capacity of the resin

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[2] It is worth noting that, with regard to the exothermic character of the curing reaction of UP resin, the hardening speed of surfacing is greatly influenced by the temperature capacity of the present filler: the greater the quantity of filler in the mix, the higher its temperature capacity, and, the amounts of the hardener and accelerator as well as the external conditions remaining the same, the slower the hardening speed, which proves, once again, the advantage of aggregated structures.

and the low thermal conductivity, however, the critical state of stress in the inner structure of the composite due to shock temperature changes will occur only rarely.

Far more serious is the effect of temperature changes on the whole composite system. The UP resin surfacing is usually placed on top of a layer of cement concrete. The difference in the coefficients of thermal expansion of both layers depends primarily on the composition of the surfacing: in the case of resin concrete with a large filler content, this difference will be small (Fig. 7).

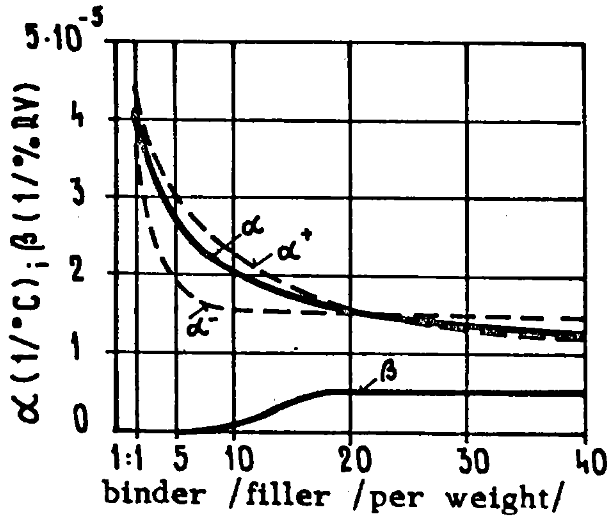

Fig. 7. Coefficient of thermal expansion for the extent of -30°C to +80°C (α), 0°C to 30°C (-α) and 0°C to 80°C (+α) and moisture expansion of UP systems.

In the case of GRP, on the other hand, thanks to the prevalence of the binder, the difference will be only slightly smaller than for the resin only. However, the thinner the layer of surfacing, the more quickly it will react to temperature changes as a whole and the less advantageous it becomes, which is the opposite to the requirement imposed with reference to shrinkage. The reduction of the temperature below the "birth" temperature is more of a disadvantage than is its increase, the effects being added to those due to shrinkage and tensile stresses in the surfacing (binder) rising; moreover, the rheological properties of the binder (relaxation and creep) are also impaired by the sinking temperature. At the contacts between different layers, the temperature changes produce considerable shear stresses, whose magnitude depends, apart from the temperature change and the difference of coefficients of thermal expansion, also on the modulus of elasticity, modulus of deformation, ultimate deformation, stress relaxation and creep of the individual layers, usually

$$(\alpha_f > \alpha_b;\ E_f < E_b;\ \left(\frac{\sigma}{\sigma_T}\right)_f > \left(\frac{\sigma}{\sigma_T}\right)_b;\ \left(\frac{\varepsilon}{\varepsilon_T}\right)_f < \left(\frac{\varepsilon}{\varepsilon_T}\right)_b,$$

where the index f denotes the flooring and the index b its base. Accordingly, a reduction of temperature (similarly as shrinkage) produces "center-bound" shear stresses of base (the surfacing is subjected to tension, its base to compression), a temperature increase producing "edge-bound" shear stresses of base (the flooring system is subjected to compression, and its base to tension).

The magnitude of shear stresses along the thickness of the surfacing (and its base) is not linear; the maximum strain is attained in the vicinity of the contact zone, sinking towards the distant boundaries of both layers (Fig. 8). In the cases of imperfect bond or lack of bond the normal stresses along the thickness of the surfacing change very little (Fig. 9); on the other hand, at the boundaries of such an unbonded spot, concentrations of horizontal shear stresses originate (Fig. 9), as is the case of any end, e.g., near the expansion joints. This provides a greater vulnerability of the surfacing in all places where its continuity (or the continuity of its bond with its base) is interrupted. For this reason it is advisable to restrict the joints in the surfacing only above the expansion joints in its base.

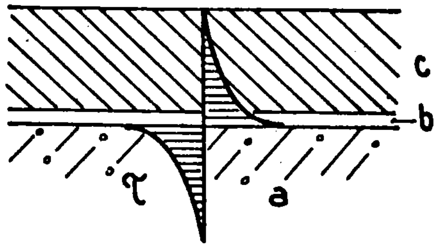

Fig. 8. Shear stresses due to temperature changes or shrinkage along the depth of the surfacing. (a) Base, (b) Contact joint (transition layer), (c) Surfacing.

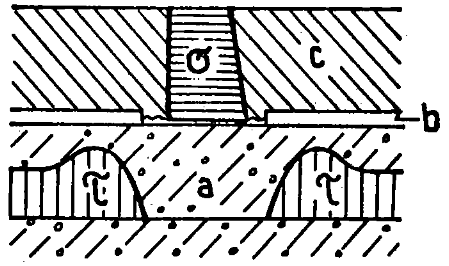

Fig. 9. Normal stresses due to temperature changes or shrinkage in the surfacing and longitudinal shear stresses in the contact joint in the place of local bond failure.

With regard to the worsening of the rheological properties of the binder (embrittlement), the effects of temperature changes become worse in the course of time.

Composite Behavior

All UP resin-based surfacings are multilayer systems or, in the case of cast surfacings, systems with nonhomogeneous density distribution along their depth. As a result of this fact, any changes described in the preceding sections (temperature changes, polymerization shrinkage) produce, with regard to the different properties of the individual layers, so-called composite behavior, i.e., mutual mechanical stressing of the individual layers followed by the bending of the system similar to the behavior of, for example, a bimetallic cell. An increase of the temperature produces concave bending accompanied by the origin of considerable tensile stresses in the contact joints between the individual layers, while a drop of the temperature results in convex lifting of the edges, whether produced technologically (expansion joints, ends, openings for the passage of pipes or other structures, working joints) or originating spontaneously as a consequence of internal stresses (cracks). Since the bond between the individual layers of the surfacing is relatively good (also due to cohesion), the failures occur first in the most vulnerable contact, the joint between the surfacing and the cement concrete base.

With regard to the magnitude of the originating stresses, even the best bond between the base and the surfacing ensured by adequate priming prior to the application of the flooring material cannot prevent failure of the joint (the separation of both layers). The only way, therefore, is to limit maximally the differences of both layers and the assimilation of the physical properties of the surfacing and the base. This aim can be ensured by the application of bonded fillers (aggregated systems) or by the selection of special resins and hardening systems, or reactive softeners. The latter method, however, brings about a number of disadvantages, the most important of which is the reduction of the hardness, wear resistance and short-term strength, which are the properties of decisive importance for surfacings with regard to their performance. Here, too, it holds that the less filler the layer contains, the thinner it should be, to limit its influence on the overall stressing of the composite. Moreover, it is advisable to arrange the flooring system always so as to make it symmetrical with regard to the central line plane; practically, this means that if a surface layer with a low filler content is applied as a top layer of the surfacing, a similar layer, in respect of composition should be applied on the opposite side of the surfacing, e.g., as a connecting layer.

Mechanical Properties

The application of a concentrated load to the surfacing produces transverse stresses which can decisively influence the usability of the flooring material. A concentrated load produces "edge-bound" shear stresses of base: the flooring system is subjected to compression, the base to tension. Of decisive importance are the moduli of elasticity (deformability) and Poisson's coefficients and the differences of the values of these quantities for the adjoining layers respectively. The greatest differences will occur between the cement concrete base and the surfacing. The greater the difference between moduli of elasticity, the higher the stresses in the contact zone produced by dynamic loading as a result of the different rate of damping. The greater the difference between the Poisson's coefficients, the higher the stresses in the contact zone produced by a concentrated load. The lower the thickness of the surfacing (down to the thinnest layer of the character of a paint coat), the greater the importance of the differences in the above mentioned quantities and the more decisive the strength of the base and the mutual bond of the individual layers. A thin layer (paint coat, a self-levelling cast compound forming a layer up to 1 mm thick) acquires the properties of its base to such an extent that unfavorable stresses produced by concentrated loads will no longer be decisive. The magnitude of the permissible (limit) concentrated (static) load for the assumed ultimate stress of the concrete base - surfacing contact joint of 1 MPa and for the assumed load distribution at an angle of 45^0 for various magnitudes of Poisson's coefficient of the surfacing is shown in Fig. 10. It can be seen that the acceptable values of the stresses in the contact joint due to the point load are attained only for the thickness of the flooring material of 2 cm. Thus, for example, for the current magnitude of $\mu = 0,30$ the ultimate static load is approximately 530 kg, which corresponds with the working load of

260 - 100 kg, according to the degree of dynamic effects. For a layer with a thickness of 5 mm and μ = 0,4 (screed) the ultimate contact stress of 1 MPa is produced by a static load of as little as 25 kg. In the case of dynamic loading, this stress is produced in the contact joint by a load of 12 - 5 kg. The thinner the layer of flooring material, the higher the strength of the base that is desirable; in the case of flooring thickness of the order of several millimeters the desirable strength of the base is 20 - 25 MPa; in the case of centimeters it is 15 - 20 MPa. The most effective way towards the increase of the mechanical load ability of the surface of the flooring material, which is sufficiently strong and hard, as a rule, is, apart from an increase of its thickness, an increase of bond of the surfacing with its base by a microscopic as well as macroscopic increase of the specific surface of the base (by sand-blasting, chipping) or by ensuring a sufficient porosity of the base surface, enabling good penetration and fixation of the priming agent, preferably by the use of porous filler. The number of indispensable characteristics of the surfacing includes, naturally, also its strength (compressive and tensile) and ultimate deformation (Fig. 11), hardness, and abrasion resistance, which grow with the increasing filler contents.

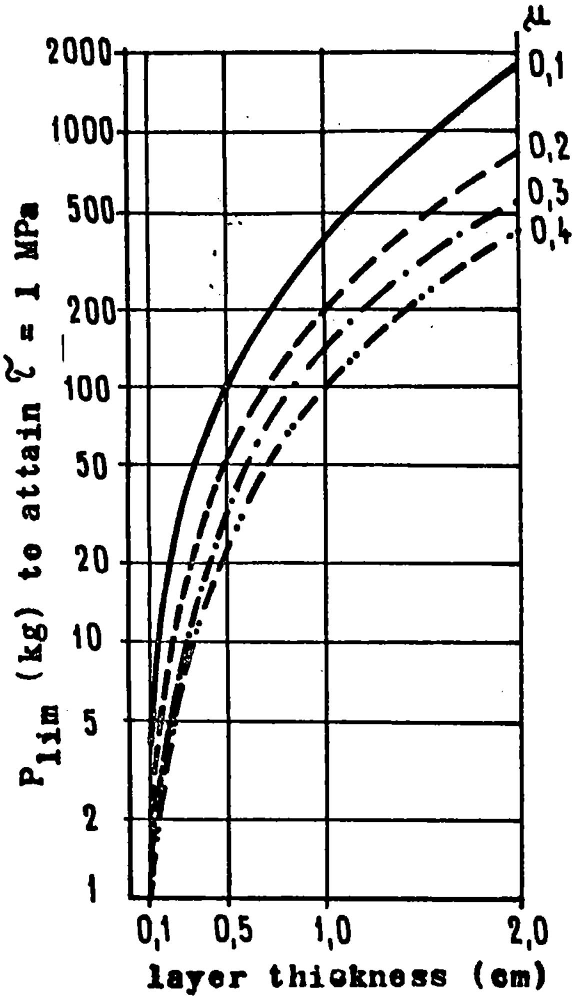

Fig. 10. Permissible concentrated load applied to the surfacing.

Structural Effects

The structure of the surfacing is influenced by its composition (the ratio and the properties of its components), processing and curing. Each of the above mentioned factors is of equal importance.

One of the principal factors influencing the quantity of the binding agent required and, consequently, all properties of the composite is the selection of the correct filler. The filler should consist of at least three gradings, including the micro-filler, and should be gap-graded, with minimum void contents, and clean, dry, and chemical resistant.

Another factor is the type of binding agent, particularly its viscosity, which determines the workability of the mix. Every modification of the viscosity by non-reactive diluters is harmful. However, even the reactive diluters should be used with utmost care only.

The influence of the mixing and the batching of the individual components as well as the homogeneity of the individual batches are not negligible, either.

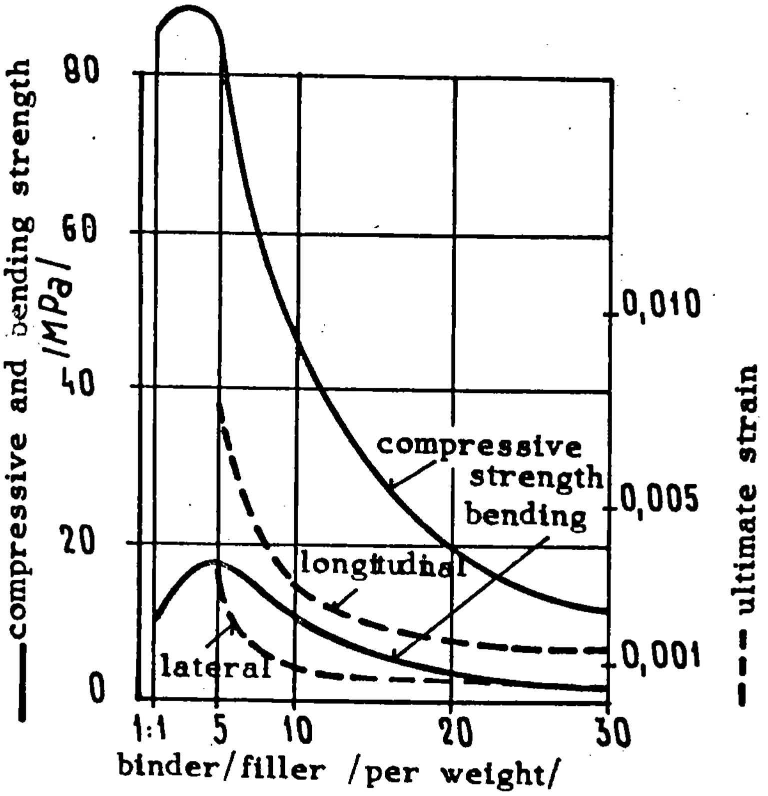

Fig. 11. Strengths and ultimate deformations of UP systems.

The ratio of both components, binder and filler, is the determining factor of the properties of the flooring material. In the majority of cases it is selected so as to ensure that the cured system, with the given method of working, should have non-continuous porosity but should have a certain amount of closed pores. In accordance with the composition and the type of components, effectiveness of mixing and curing, this ratio varies between the limits of 1:6 and 1:11, most frequently between 1:7 and 1:8 per weight.

The properties of the surfacing are considerably influenced by the conditions of the environment in which the working and the curing of the material take place (the "birth" temperature); both a high and a low temperature are harmful, as is a high moisture content.

Moisture Content of Raw Materials, Base, and Environment

UP resins are very sensitive to moisture. Water, even in minute quantities, acts as inhibitor to the polymerization reaction and cannot only decelerate or even entirely prevent curing, but can also give rise to subsequent unfavorable chemical reactions.

When filler is used, whether granular or fibrillate, it must be dry, i.e., it must not contain more than 0.3 percent of water by weight.

The moisture content of the base, naturally, also plays a role of great importance in the process of curing the UP surfacing, particularly in the initial phase. The humidity can be stationary (primary, induced into the base) or dynamic (secondary, originating in the atmosphere, external humidity). It can be present in the whole system in a liquid form (water solution) and/or in the form of water vapor near the state of saturation.

The curing is inhibited also by the oxygen from the atmosphere; if the air is moist, the inhibition is even more effective. In extreme cases, the hardening of the surface layer may be entirely prevented (see "Chemical Factors").

Humidity in the form of condensed water, or water solution, may exercise an unfavorable influence in the physical sense also - first by its cleavage effect at the boundaries of solid phases in the structure and particularly at the boundaries of different layers of the composite system. In cases in which the surfacing may be exposed to frost, the effect of water present below any layer of the structure is obviously detrimental.

The moisture conditions in a floor system become considerably more complicated under the effect of a temperature gradient due to a radiant heating system built into the floor structure. If the heating system is situated near the lower surface of the structural slab, the circulation of moisture towards the upper, cooler, surface is facilitated.[3] The temperature gradient may be considerable, from 55°C at the lower surface to the temperature of outside air at the upper surface, in the case of ventilation of the upper room or below the roof. The gradient of 0 to 55°C in winter need not be exceptional. Apart from great stresses in all contacts and all parts of the floor system, radiant heating influences intensively also the pressure of vapors and the diffusion and transport of moisture in the floor system. The circulating vapors, directed by the temperature gradient towards the upper surface of the system, encounter there a practically impermeable barrier.

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[3] The individual layers below the surfacing, with the exception of the damp proof course, are capable of passing quantities of vapors of a several times higher order, by weight, than surfacing. A temperature rise of 30°C produces in the system an air (vapor) overpressure of some 20 kPa (3). The vertical flow of vapors through the surfacing for a temperature of heating water of 60°C is of the order of 0.001 Pa/h or less, while the same property of concrete is of the order of 0.015 Pa/h.

An overpressure originates below the surfacing, condensation takes place, and the vapors and liquid penetrate into the lower strata of the surfacing. In the case of resin concrete, they physically as well as chemically disturb its structure. Similarly in the case of a surfacing reinforced with glass fibers the liquids follow the fibers or minor local failures and penetrate as far as the top layer, where they compress until the upper strata yield to this pressure; local cleavage of the bearing and the surfacing layers ensues (Fig. 12).

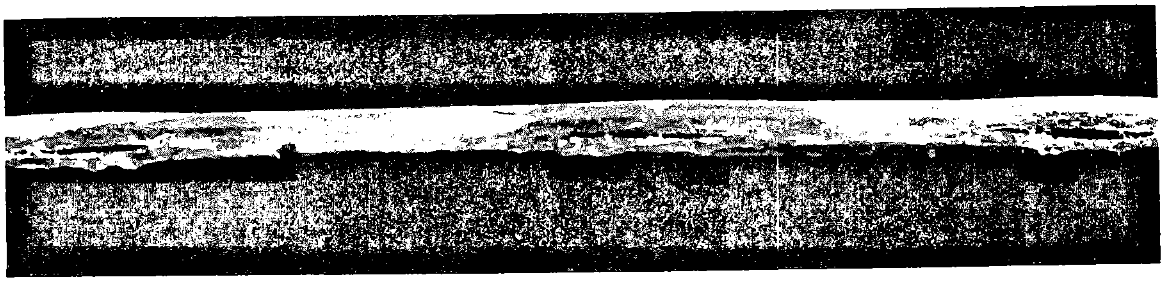

Fig. 12. Cleavage of permeable and impermeable layers of a GR - UP system due to vapor overpressure (cross section of the surfacing).

Further development is causal: the pressure increases again; in weaker spots blisters appear (see Fig. 4); the upper strata becomes deformed; and the vapors and liquids concentrate in these places, relieving the adjoining areas. The blisters increase until the pressure conditions become balanced, i.e., until the upper layer of the surfacing separates from the base over a greater area or until failure occurs, i.e., until the blister is punched, thus letting the vapors and liquids loose.

A role of great importance in this process is played by the physical and mechanical properties of the surfacing subjected to long-term loads at higher temperatures, possibly also to the chemical effects of some (even destructive) components. The creep of the surfacing under such circumstances is considerable and a relatively low overpressure may result in the origin and increase of blisters. Outside the heating season, in approximately isometric conditions, on the other hand, the moisture exchange between the system and its environment is determined by the moisture gradient at the interface only.

The only effective method of preventing the diffusion of vapors from the lower to the upper surface due to the non-equilibrium of moisture conditions above and below, or in, the floor system is a damp proof, and vapor proof, course situated as near the impermeable surfacing as possible, i.e., below the concrete base.

The air inhibition can be limited by an admixture of, for example, parafinic components to the upper layer of the surfacing.

Aging

It has been mentioned several times already that with the growing time elapsed from the placing of the UP surfacing, its elasticity and pliability decrease, the resin becoming brittle. The ratio of the tensile to compressive strengths decreases; the impact strength decreases similarly as the permanent strength. These phenomena manifest themselves most markedly in the case of exposure to ultraviolet radiation, whose effect may cause a degradation of the UP resin accompanied by a reduction of its strength, which can border on a complete disintegration of the surfacing.

The relatively speedy aging of plastics is well known and must be considered as one of their specific properties. The reduced possibility of relaxation often results in the failures of the system after the elapse of a considerable period from its production. There is no other way than respecting the properties of the binding agent (resin) used in the selection of stresses.

The unfavorable effect of ultraviolet radiation on UP resins is considerably reduced in systems of bonded fillers, the PC type[4], sharply contrasting in this respect with filled binders, e.g., screeds. For practical exterior application, therefore, only such bonded filler systems can be approved whose binder: filler ratio is only slightly below the permeability limit. Particularly careful execution is desirable here, as the criteria of frost resistance and non-absorptivity require impermeability of the system. For exterior application, there is only a very narrow range of mutual binder: filler ratio. Naturally, it is impossible to apply a surfacing layer of slightly filled resin on top of a PC base.

Base Treatment

The importance of the proper treatment of the base which is to receive a UP surfacing cannot be overestimated. If a poor quality concrete base surface, consisting of the lightweight particles of cement and aggregate, is not removed first, this layer becomes an integral part of the surfacing after priming and the contact zone will originate between this layer and the sound concrete; the bond between the two layers being minimal. If the base is strong and non-absorbing, it is impossible to circumvent the measures increasing the effectiveness of the bond of the surfacing to the base, e.g., the increase of the specific surface by means of sandblasting or some similar process. If the base has a sufficiently large open inner surface, it is absorbent and the priming must penetrate to a sufficient depth. Perfect penetration of the binding agent of the surfacing, or some other compatible material capable of chemical bond with the binding agent of the surfacing, into

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[4] i.e., in the systems where the filler is aggregated, or, in other words, in the systems with the binder:filler ratio in excess of approximately 1:8.

the structure of the base will enable the distribution of shear stresses from one plane into the whole zone. Penetration is necessary to ensure utilization of the mechanical properties of the base to the full extent; therefore, the contact joint must have a shear strength (tensile strength) which is higher than, or at least equal to, that of the base.

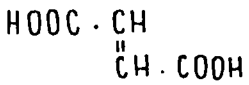
To ensure the full effectiveness of penetration priming, the base surface must be dry, i.e., its pores must be empty and capable of filling with resin; the diluter used in the priming solution must be so selected as to enable the penetration of the resin to the assumed depth before its evaporation. Neglecting to follow these principles (priming of a wet surface, use of speedily evaporating diluters, such as acetone) results in the formation of a thin surface layer not bonded with the base.

In any case, it is necessary to check whether the diffusion of vapors through the base to the surfacing and their possible condensation in the contact zone have been prevented. This applies to both the moisture transported from the base, or atmosphere, and that introduced into the floor system by the technological process or in some other way, e.g., accidentally. In a balanced moisture content of the base and other lower courses above the damp proof course (e.g., when the base is placed on the soil or above rooms with highly moist atmosphere), or of all layers of the floor system, if no damp proof course is used, failures of the flooring material, whether they are due to chemical or physical factors, necessarily occur.

CHEMICAL FACTORS

Influence of Moisture

We have already mentioned the fact that UP resins are undesirably sensitive to water, whose effect on the finished polymer was discussed in a preceding section. In this section, the effect of water on the actual curing process in discussed.

Inhibition -- Water present in the material during the polymerization process acts as an inhibitor of the polymerization reaction by lessening the effect of the initiator, thus reducing the speed of the reaction. Deceleration of the polymerization can mean that the curing process may not be fully completed and that the resulting material comprises monomers which interfere with it in some way or other. For example, in extracts of faulty PC produced using organic solvents, the presence of an excessive quantity of monomeric (non-polymerized) styrene and fumaric acid  $\begin{matrix}HOOC\cdot CH\\ \| \\ CH\cdot COOH\end{matrix}$ was ascertained. In a fully cured polyester, both of these components must be mutually covalently bound in a polymeric, inextractable form. Laboratory experiments with artifically prepared model mixes have revealed that the presence of water indeed prolongs the curing: 3 percent moisture by weight of the sand (i.e., 25 percent by weight of the resin quantity) to 10 days and over. On the other hand, it has been ascertained that moisture does not consistently hinder the cross linking of the polymer and acts rather as an internal lubricator, or secondary softener (Fig. 13). Therefore, water introduced into the mix does not seem by itself to be the cause of the resin concrete failures as a rule.

Oxidation -- The second negative feature of slow polymerization is the fact that further disturbing chemical factors may exercise a more marked influence, which are not felt in the course of a normally uninhibited and speedily propressing cross linking (e.g., the effect of oxygen). The oxidation by atmospheric oxygen or by oxygen dissolved in and carried by water occurs always, but the time of exposure to the effect of oxygen of non-polymerized resin is obviously decisive for the properties of the polymer; a relatively long curing period may result in defects. Slow curing, however, may also be due, apart from the inhibition by water, to the shortage of hardener or accelerator or to the excessive quantity of the reactive styrene monomer which is often undesirably introduced to improve the workability of the mix.

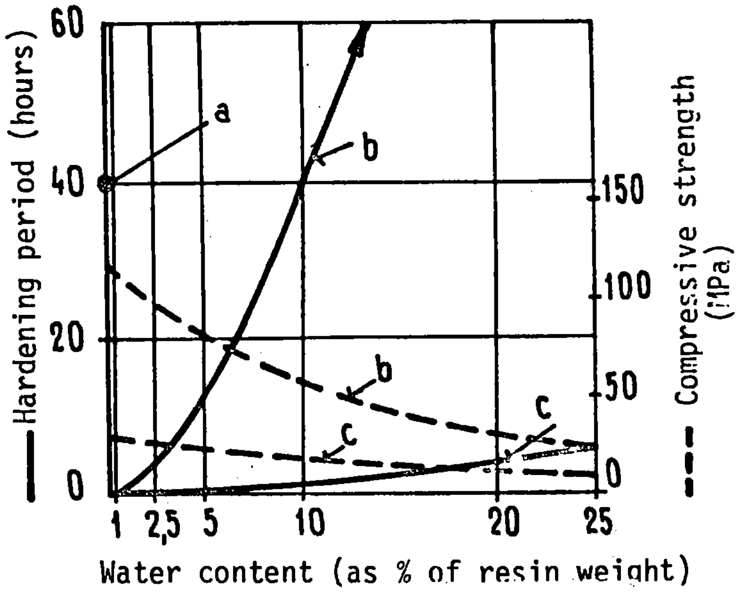
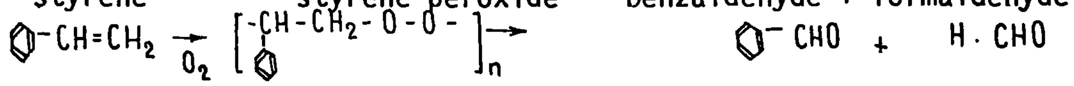


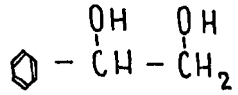
Fig. 13. Influence of the water contents in the curing UP resin on the curing time and strength. (a) without accelerator, 4% of hardener; (b) 1.5% of accelerator, 4% of hardener; (c) 1.5% of accelerator, 20% of hardener.

When investigating the causes of several failures of PC surfacings, the presence of styrene oxidation products was ascertained, which proved that oxidation does occur and that the styrene is oxidized instead of being built into the originating duroplastic net. An important indicator of the oxidation is the presence of benzaldehyde in the faulty polymer. Benzaldehyde originates by the oxidation of styrene:



Because of the intense odor of styrene, it can be sometimes proved in a failed surfacing by smell. Styrene peroxide as an intermediate product of oxidation can also be polymeric and its origin may produce the impression of set, which, naturally, is only temporary. The benzaldehyde and other substances produced by oxidation alone are further inhibitors of the polymerizing reaction. The process is irreversible; in a system impaired by oxidation it is impossible to renew the polymerization in any way (not even by introduction of new resin with the necessary admixtures), which is very unfavorable for possible repairs.

Another compound which can be proved in a failed surfacing is the phenylethyleneglycol



$C_6H_5-CH(OH)-CH_2(OH)$

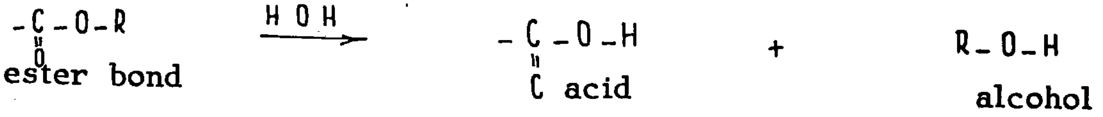
whose origin can be also explained by the oxidation of styrene. The artificial origin of this substance in a relatively large quantity was reproduced in a laboratory by mixing monomer resin with wet sand of about 3 to 4 percent of moisture content and leaving the mix spread, exposed to air, for about a week. The sample did not set and in appearance it resembled in many aspects the failed PC. The resin along (without moist sand) with the corresponding quantity of water (25 percent by weight of the resin) hardened in a week (Fig. [illegible]) and showed a compressive strength of 29.0 MPa after three months. On the other hand, not even a ten-fold increase of the amount of hardener (peroxide) during polymerization resulted in the origin of phenolethylene glycol.

The quantity of oxygen in the batch during its preparation (as oxygen occluded on sand particles, diluted in water, introduced into the mix during its mechanical mixing) probably is sufficient to attack, in a slow and insufficient polymerization process, the matter capable of oxidation, particularly the non-polymerized styrene. The oxidation can be fostered effectively also by insufficient working (compaction) of the mix. The oxidation may proceed, naturally, even after the surface has been covered with a hard protection coat if a sufficient quantity of oxygen remains below.

Moreover, the lower insufficiently polymerized substances and monomers are capable, as is any organic solvent, of damaging the structure of PC by their effects; they act as softeners and they soften themselves, increase their volume, and produce internal pressures.

<u>Hydrolysis</u> -- The polymer structure contains also ester bonds, e.g., between adipic acid $HOOC(CH_2)COOH$ or phthalic acid

and glycols, which can be hydrolyzed by the effect of water, particularly in the presence of alkali, producing organic acids and alcohol.



$$\underset{\text{ester bond}}{-\overset{}{\underset{\|}{\underset{O}{C}}}-O-R} \xrightarrow{HOH} \underset{\text{acid}}{-\underset{\|}{\underset{C}{C}}-O-H} + \underset{\text{alcohol}}{R-O-H}$$

The fumaric acid is built into the polymeric network through the molecules of styrene by means of another than ester bond and, therefore, is not subject to hydrolysis. If hydrolysis of ester bonds of UP occurred to a major extent, the failed (softened) polymer should contain the phthalic or adipic acid but not the fumaric acid, and free glycols.

In the cases of failures due to the formation of blisters below the upper layer (see Fig. 12) filled with liquid, the decisive role of water in the damage to the surfacing was proved, primarily due to its mechanical (physical) effects. The chemical analyses of the liquids from the blisters have shown that hydrolysis also plays a role. Water with dissolved calcium salts (e.g., in the form of acid carbonate) and alkali metals (e.g., kalium carbonate) not only effects the surfacing mechanically but also causes (in some cases even under pressure) hydrolysis, particularly of the less polymerized parts of the polyester, dissolves part of the hydrolysis products, and transports them into blisters. The presence of organic acids and glycols in the blister liquid has been proved; both types; both types of substances are bound to the ions of calcium in one way or other.

Degradation and depolymerization -- Proofs of a direct disintegration of correctly linked polyesters due to water have not been found so far. It is natural that degradative processes proceed in every polymer continuously; however, their rates are so low that they do not manifest themselves in the properties of the macro molecules. It can be assumed that, if the polymeric structure has already been disturbed in some way, the degradation processes (primarily oxidation), as well as the processes of direct depolymerization, can proceed more speedily. Apart from water, the cause of the degradation can also be other low molecular substances and manifest itself by swelling, increase of volume, and loss of strength.

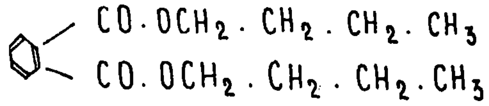
Effects of Technology of Batch Preparation

Raw materials -- The purity and quality of raw materials used is also of great importance. All organic components have a limited stability and they gradually become inactive. The hardener is a particularly sensitive component in this respect, its active oxygen sinking relatively quickly; after prolonged or inadequate storage it becomes entirely unusable. Impurities contained in monomers, if not taking part in polymerization, may act (similarly to the oxidation products) as chemical and mechanical inhibitors and disturb, also, the cohesion of polymers.

The bearer of inhibition properties can also be unsuitable sand, containing for example, zinc dioxide, too many quartzites, or carbonates; during the drying of sand its further contamination by soot, phenols, oils, etc. is possible.

When zinc white is used (as white pigment) instead of titanium white or when unsuitable titanium white (anatase or coarse-ground rutile white) is used, curing is impaired. Analogous is the effect of an admixture of chromium oxide if it is not treated with aluminum oxide.

Incorrect components ratio -- An insufficient amount of the building agent is not among direct chemical effects but is often the cause of low strength of PC. It can manifest itself as a spatially limited local shortage of binder (due, for example, to insufficient mixing of the materials) or can have the character of an overall failure (due to an error of batching). The shortage of hardener and accelerator reduces the curing speed, which can give rise to complications from oxidation. Many tests of samples taken from floorings which have shown the signs of defects or failure have proved, among other things, considerable nonhomogeneity of the mix. The local quantities of the hardener were determined by the determination of the dibutylesther of phthalic acid



which is a part of the hardener and has practically identical chemical and physical stability with that of the originating polyester polymer. The quantity of accelerator was determined by the quantity of cobalt in the PC ashes. Similarly to an insufficient quantity of hardener and accelerator, an excess of styrene in the mix, used to improve its workability, has a harmful effect.

MICROBIOLOGICAL FACTORS

If the surfacing or floor system affords suitable climatic and nutrition conditions, there is the danger of microbiological corrosion. In this respect, particularly, the predominance of high moisture content, combined with a high temperature (originating, for example, when radiant floor heating is used) fosters the development of microorganisms to which the surfacing or floor systems usually afford sufficient nutrition (3).

From the number of molds which can be expected, and whose occurrence has been ascertained in some concrete cases, mention should be made, particularly, of rhizopus nigricans, penicillium brevicompactum, penicillium chrysogenum, penicillium sp., aspergillus fumigatus, aspergillus clavatus, aspergillus Amstelodami, paecilomyces varioti, and alternaria tenuis.

Apart from their microbiologically corrosive effect some types are also pathogeneous for man; therefore, their occurrence must be considered particularly dangerous. In some cases the growth of molds may be stimulated even by some component of the flooring material, e.g., unsuitable finishing of glass fibers.

CONCLUSION

UP resin surfacing, if correctly batched, mixed, produced, and polymerized, and if not used in a moist, alkali environment, are very good and economical even for heavy traffic and have a good aesthetic effect and a high life expectancy. On the other hand, UP systems require, more than any others, perfect observance of production technology and a thorough knowledge of all circumstances influencing their properties. Failure to observe these requirements often leads to various defects and failures. The analysis of the causes of various defects of UP systems may prove useful for both the design and the execution. The requirements imposed on the selection of the system are often contradictory (e.g., the requirements of the highest speed of polymerization to prevent oxidation versus the requirements of slow curing to prevent high shrinkage stresses). It is obvious that no universal, generally applicable guidelines can be given. On the contrary, on the basis of a thorough analysis of concrete conditions and requirements it is necessary to select a particular, optimum composition and technology to suit every particular case.

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